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THE PRIMARY FACTORS IN
PETROLEUM EMULSIONS
—♦♦♦—
FRANK MICHAEL TULLY

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The Primary Factors in Petroleum Emulsions

By

Frank Michael Tully *
B.S. (United States Naval Academy) 1942

THESIS

Submitted in partial satisfaction of the requirements for the
degree of

MASTER OF SCIENCE

in

Petroleum Engineering

in the

GRADUATE DIVISION

of the

UNIVERSITY OF CALIFORNIA

JUNE 1948

Approved:

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THE UNIVERSITY OF CHICAGO

PH.D. THESIS

1993

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CHICAGO, ILLINOIS

IN

DEPARTMENT OF PHYSICS

BY

DAVID J. GRIFFIN

1993

CHICAGO, ILLINOIS

1993

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1993

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Gratitude is due the University of California for the use of its laboratories and libraries both in the Petroleum Engineering and Chemistry Departments. The advice of the faculty and their willing cooperation were of great assistance. Appreciation is also expressed of the opportunity afforded by the United States Navy to accomplish the thesis.

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THE PRIMARY FACTORS IN PETROLEUM EMULSIONS

Introduction

In order to form a stable emulsion of two immiscible or partially immiscible liquids, a third substance, an emulsifying agent, must collect at the interface, form a coherent film about the globules of the dispersed phase and thereby prevent coalescence. This is held by Dodd¹ et al. The asphaltic constituent in petroleum and its derivatives is a native emulsifying agent. Sherrick,² and Lottermoser and Calantar³ emphasize the importance of asphaltic matter as the emulsifying agent. Emulsions can be broken by removing the asphaltic material by any of several means: by adsorption with fuller's earth, by extraction with alcoholic sodium hydroxide, or by precipitation by anhydrous stannic chloride. Dow and Reistle⁴ found that oil recovered from emulsions had higher carbon residue values than the unemulsified portion of the same oil, which indicated that the asphaltic components had concentrated in the emulsion.

The interfacial tension between the oil and the water globules and the extent to which the emulsifying agent changes the interfacial tension are important factors in emulsibility. Lowering of the tension between the liquid phases promotes emulsification; raising of the interfacial tension

DEPARTMENT OF THE ARMY, WASHINGTON, D. C.

and slowly turning clockwise. This is held in place

² The formula is $\frac{1}{2} \pi \frac{1}{\sin \theta} \frac{d\sigma}{d\Omega} \frac{d\Omega}{d\theta}$ for θ and $\frac{d\Omega}{d\theta}$ in radians.

favors demulsification. Different agents have varying degrees of emulsifying power. The addition of soap to oil and water decreases the interfacial tension and increases emulsification, while such chemicals as are used to break petroleum emulsions increase the interfacial tension. The compositions of the two liquids are also important factors in emulsification, inasmuch as the interfacial tension between solvents differs and, as found by the author, a given emulsifier will have differing effect upon the interfacial tension between any two particular solvents. Hence, petroleum products, which are ordinarily mixtures of several hydrocarbons, have interfacial tensions with water dependent on their composition. That the composition of an oil affects the emulsibility of the oil was hinted by Katz and Ben,⁵ "One view could be that the asphaltenes are 'potential colloids' and that solutions containing them easily convert into colloidal systems from changes in the composition of the solution." Hellensteyn⁶ found that the addition of liquids, which have a surface tension below 24-26 dynes/cm. at 25° C., causes flocculation of the asphaltic micelle, while the addition of liquids having a surface tension above 26 dynes/cm. causes peptization.

Even the impurities in the water affect the interfacial tension of the system. So also does the composition of the asphaltic matter. For example, in this work it was found

former condition. With these results have varying the

system of condensing power. The addition of soap to oil

and water condensed the industrial machine and increased

emulsification, while some specimens are now used to treat

particular emulsions because the industrial machine. The

composition of the oil itself has also important factors

in emulsification, because as the industrial machine is

used various different oils, as found by the author, it gives

emulsions which have different effects upon the industrial

machine. Some of the results are as follows.

Various emulsions, which are especially suitable for emulsions of emulsions

emulsions, have industrial machine with other emulsions

in their composition. The composition of an oil is

found the emulsification of the oil was found by the author

and the results are as follows. The results are as follows

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into emulsions and the results are as follows. The results are as follows

the emulsions. The results are as follows. The results are as follows

emulsions, which have a certain amount of emulsification

at 25° C., caused emulsification of the emulsions machine.

With the addition of certain factors a certain amount

may be seen. The results are as follows.

From the results in the water effect the industrial

emulsion of the system is also seen the composition of the

emulsion itself. The results are as follows. The results are as follows

that cracked asphaltic matter on a weight basis lowered the interfacial tension more than did straight-run asphaltic matter, all other factors being equal. The structure and molecular weight of the asphaltic matter, the extent to which it has been oxidized, the radical groups attached, the molecular polarity,—all influence the effect of the asphaltic matter on the interfacial tension of the system.

In any one system, however,—composed of an oil of given hydrocarbon composition, water of given impurity content, and asphaltic matter of given composition—there is a definite interfacial tension at a particular temperature. This interfacial tension is an important factor in the emulsibility of the system, i.e., the ability of the system to remain emulsified. Systems having high interfacial tensions are thermodynamically unstable, since their resolution results in a decrease of interfacial area and free energy of the system. Hence, high interfacial tension promotes coalescence of the dispersed phase and thence demulsification. Conversely, the lower the interfacial tension of the system, the more stable is the emulsion.

Primarily involved in emulsibility is the sedimentation force. There are two opposing forces acting vertically: the effective force of gravity (or centrifugal force should it be applied) and the kinetic force of diffusion. The effective force of gravity allows for the buoyancy of the oil, and for one mole of suspended particles is:

1. The first step in the process of the investigation is the identification of the problem. This is done by the investigator who is assigned to the case. The investigator will then gather information about the problem and the individuals involved. This information will be used to develop a hypothesis about the cause of the problem. The hypothesis will then be tested by the investigator. If the hypothesis is proven to be correct, the investigator will then develop a plan to solve the problem. If the hypothesis is proven to be incorrect, the investigator will then develop a new hypothesis and test it. This process will continue until the problem is solved.

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that, beyond having that important demand for the
the system, the ability of the system to handle multi-
channel demand is an important factor in the evaluation of
channel demand as a potential demand. The inter-

[illegible]

and for one more of suggested material is

$$P_{\text{gravity}} = N g v \Delta \rho \quad (1)$$

where N is Avogadro's number, g is the gravitational acceleration, v is the average volume of the water particles, and $\Delta \rho$ is the difference in density between the water and oil. This force endeavors to pull the water particles to the bottom of the vessel and increase the concentration of water particles there. Opposing this force is the Brownian kinetic force which causes the colloidal particles to diffuse from a region of higher concentration to one of lower concentration, i.e., upward. The change in free energy ΔF when one mole of water particles diffuses from concentrations n_1 to n_2 is given by

$$\Delta F = RT \ln \frac{n_2}{n_1} \quad (2)$$

The average kinetic force causing diffusion then is

$$P_{\text{diffusion}} = \frac{RT}{x_1 - x_2} \ln \frac{n_2}{n_1} \quad (3)$$

where $x_1 - x_2$ is the distance between the points of concentration n_1 and n_2 . Values of n_1 and n_2 may be determined by counting the number of particles in a given field of a microscope. The net force, or sedimentation force, at any time is therefore

$$P_{\text{sed}} = P_{\text{grav.}} - P_{\text{diff.}} \quad (4)$$

$$= N g v \Delta \rho - \frac{RT}{x_1 - x_2} \ln \frac{n_2}{n_1} \quad (5)$$

When the emulsion has reached equilibrium the sedimentation force will be zero and

$$N g v \Delta \rho = \frac{RT}{x_1 - x_2} \ln \frac{n_2}{n_1}$$

or $\ln \frac{n_2}{n_1} = \frac{N g v (x_1 - x_2) \Delta \rho}{RT}$ (6)

Viscosity is also a factor in emulsibility. The rate of diffusion is dependent on the viscosity according to

$$D = \frac{RT}{N 6 \pi \eta r} \quad (7)$$

where D is the specific rate of diffusion, η is the coefficient of viscosity of the continuous phase, and r is the radius of the spherical water particle. The greater the viscosity, the less will be the diffusion of the colloidal water particles upward, and sedimentation downward will be increased. Thus viscosity, by retarding diffusion upward, tends to decrease the emulsibility. On the other hand, water globules, which have coalesced and are of sufficient size as to be unaffected by Brownian kinetic forces and which tend to settle out under the effective force of gravity, are retarded from doing so by viscosity. According to Stokes' law this frictional force is

$$f = 6 \pi \eta r \quad (8)$$

In this instance, viscosity tends to increase the emulsibility by retarding the settling of coalesced water particles. Viscosity is a frictional force and always opposes motion, whether it be colloidal diffusion upward or the settling of coalesced globules downward. It is also significant that

$$\frac{100}{100} \text{ m.c. } \frac{100}{100} \text{ m.c. } = 9.2 \text{ m.c.}$$

$$(3) \quad \frac{9A \ln(1+2) \cdot 2^2}{24} = \frac{9A}{12} \ln 4 = 3A \ln 4$$

Uspensky is also a feature in our study.

10-10-1964

(7) $\frac{1}{2} \pi$ 0.0

where U is the overall rate of utilization, in the case

[illegible]

medium of the experiment was water. The results are also

...the fact that the ...

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any of the other conditions to which New Guinea was subjected

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and under the following conditions of matter are intended from

(5) $\pi \pi \pi \pi$

...and the ...

1999, 2000, 2001, 2002, 2003, 2004, 2005, 2006, 2007, 2008, 2009, 2010, 2011, 2012, 2013, 2014, 2015, 2016, 2017, 2018, 2019, 2020, 2021, 2022, 2023, 2024, 2025, 2026, 2027, 2028, 2029, 2030, 2031, 2032, 2033, 2034, 2035, 2036, 2037, 2038, 2039, 2040, 2041, 2042, 2043, 2044, 2045, 2046, 2047, 2048, 2049, 2050, 2051, 2052, 2053, 2054, 2055, 2056, 2057, 2058, 2059, 2060, 2061, 2062, 2063, 2064, 2065, 2066, 2067, 2068, 2069, 2070, 2071, 2072, 2073, 2074, 2075, 2076, 2077, 2078, 2079, 2080, 2081, 2082, 2083, 2084, 2085, 2086, 2087, 2088, 2089, 2090, 2091, 2092, 2093, 2094, 2095, 2096, 2097, 2098, 2099, 2100, 2101, 2102, 2103, 2104, 2105, 2106, 2107, 2108, 2109, 2110, 2111, 2112, 2113, 2114, 2115, 2116, 2117, 2118, 2119, 2120, 2121, 2122, 2123, 2124, 2125, 2126, 2127, 2128, 2129, 2130, 2131, 2132, 2133, 2134, 2135, 2136, 2137, 2138, 2139, 2140, 2141, 2142, 2143, 2144, 2145, 2146, 2147, 2148, 2149, 2150, 2151, 2152, 2153, 2154, 2155, 2156, 2157, 2158, 2159, 2160, 2161, 2162, 2163, 2164, 2165, 2166, 2167, 2168, 2169, 2170, 2171, 2172, 2173, 2174, 2175, 2176, 2177, 2178, 2179, 2180, 2181, 2182, 2183, 2184, 2185, 2186, 2187, 2188, 2189, 2190, 2191, 2192, 2193, 2194, 2195, 2196, 2197, 2198, 2199, 2200, 2201, 2202, 2203, 2204, 2205, 2206, 2207, 2208, 2209, 2210, 2211, 2212, 2213, 2214, 2215, 2216, 2217, 2218, 2219, 2220, 2221, 2222, 2223, 2224, 2225, 2226, 2227, 2228, 2229, 2230, 2231, 2232, 2233, 2234, 2235, 2236, 2237, 2238, 2239, 2240, 2241, 2242, 2243, 2244, 2245, 2246, 2247, 2248, 2249, 2250, 2251, 2252, 2253, 2254, 2255, 2256, 2257, 2258, 2259, 2260, 2261, 2262, 2263, 2264, 2265, 2266, 2267, 2268, 2269, 2270, 2271, 2272, 2273, 2274, 2275, 2276, 2277, 2278, 2279, 2280, 2281, 2282, 2283, 2284, 2285, 2286, 2287, 2288, 2289, 2290, 2291, 2292, 2293, 2294, 2295, 2296, 2297, 2298, 2299, 2300, 2301, 2302, 2303, 2304, 2305, 2306, 2307, 2308, 2309, 2310, 2311, 2312, 2313, 2314, 2315, 2316, 2317, 2318, 2319, 2320, 2321, 2322, 2323, 2324, 2325, 2326, 2327, 2328, 2329, 2330, 2331, 2332, 2333, 2334, 2335, 2336, 2337, 2338, 2339, 2340, 2341, 2342, 2343, 2344, 2345, 2346, 2347, 2348, 2349, 2350, 2351, 2352, 2353, 2354, 2355, 2356, 2357, 2358, 2359, 2360, 2361, 2362, 2363, 2364, 2365, 2366, 2367, 2368, 2369, 2370, 2371, 2372, 2373, 2374, 2375, 2376, 2377, 2378, 2379, 2380, 2381, 2382, 2383, 2384, 2385, 2386, 2387, 2388, 2389, 2390, 2391, 2392, 2393, 2394, 2395, 2396, 2397, 2398, 2399, 2400, 2401, 2402, 2403, 2404, 2405, 2406, 2407, 2408, 2409, 2410, 2411, 2412, 2413, 2414, 2415, 2416, 2417, 2418, 2419, 2420, 2421, 2422, 2423, 2424, 2425, 2426, 2427, 2428, 2429, 2430, 2431, 2432, 2433, 2434, 2435, 2436, 2437, 2438, 2439, 2440, 2441, 2442, 2443, 2444, 2445, 2446, 2447, 2448, 2449, 2450, 2451, 2452, 2453, 2454, 2455, 2456, 2457, 2458, 2459, 2460, 2461, 2462, 2463, 2464, 2465, 2466, 2467, 2468, 2469, 2470, 2471, 2472, 2473, 2474, 2475, 2476, 2477, 2478, 2479, 2480, 2481, 2482, 2483, 2484, 2485, 2486, 2487, 2488, 2489, 2490, 2491, 2492, 2493, 2494, 2495, 2496, 2497, 2498, 2499, 2500, 2501, 2502, 2503, 2504, 2505, 2506, 2507, 2508, 2509, 2510, 2511, 2512, 2513, 2514, 2515, 2516, 2517, 2518, 2519, 2520, 2521, 2522, 2523, 2524, 2525, 2526, 2527, 2528, 2529, 2530, 2531, 2532, 2533, 2534, 2535, 2536, 2537, 2538, 2539, 2540, 2541, 2542, 2543, 2544, 2545, 2546, 2547, 2548, 2549, 2550, 2551, 2552, 2553, 2554, 2555, 2556, 2557, 2558, 2559, 2560, 2561, 2562, 2563, 2564, 2565, 2566, 2567, 2568, 2569, 2570, 2571, 2572, 2573, 2574, 2575, 2576, 2577, 2578, 2579, 2580, 2581, 2582, 2583, 2584, 2585, 2586, 2587, 2588, 2589, 2590, 2591, 2592, 2593, 2594, 2595, 2596, 2597, 2598, 2599, 2600, 2601, 2602, 2603, 2604, 2605, 2606, 2607, 2608, 2609, 2610, 2611, 2612, 2613, 2614, 2615, 2616, 2617, 2618, 2619, 2620, 2621, 2622, 2623, 2624, 2625, 2626, 2627, 2628, 2629, 2630, 2631, 2632, 2633, 2634, 2635, 2636, 2637, 2638, 2639, 2640, 2641, 2642, 2643, 2644, 2645, 2646, 2647, 2648, 2649, 2650, 2651, 2652, 2653, 2654, 2655, 2656, 2657, 2658, 2659, 2660, 2661, 2662, 2663, 2664, 2665, 2666, 2667, 2668, 2669, 2670, 2671, 2672, 2673, 2674, 2675, 2676, 2677, 2678, 2679, 2680, 26

the viscosity of an oil is increased by the presence of colloidal asphaltic matter, as pointed out by Lottermoser and Calantar.³

The asphaltic constituents of an oil are macromolecular mixtures of aromatic and naphthenic rings with paraffinic side chains.⁷ Straight-run asphaltic matter is mainly composed of naphthene rings which are susceptible of dehydrogenation to aromatic rings. Under relatively severe conditions asphaltic matter may be oxidized to saponifiable products.

Solubility tests are used to divide asphaltic materials into different classes. Richardson's⁸ system classifies them in their order of decreasing solubilities: maltenes, resins, asphaltenes, carbenes, and carboids. Maltenes are soluble in light petroleum naphtha (88°). Resins are a part of the maltene fraction; they are soluble in light naphtha but may be recovered from it by adsorbents such as fuller's earth. Asphaltenes are insoluble in light naphtha but soluble in benzene. Carbenes are insoluble in benzene and carbon tetrachloride but soluble in carbon disulfide. Carboids are insoluble in carbon disulfide.

Carbenes and carboids are present, if at all, in petroleum products to a very minor degree. Maltenes are soluble in the various products. Hence it is the asphaltenes and resins that constitute the bulk of the asphaltic matter which acts as

Initial negative results, as indicated by the following text:

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... because and especially the present, it is all, in particular
... to a very great degree. ... the
... . Hence it is the responsibility and the task of
... of the scientific method with an

emulsifying agent. They are colloidal in size, are adsorbed at the water-oil interface, forming a unimolecular film,⁹ probably aided by their polarity if they have been oxidized.

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Statement of Experimental Work

The role of asphaltenes as the emulsifying agent in water-in-oil emulsions was investigated from a number of different viewpoints. The experimental work was divided into four parts:

I. A comparison was made of the abilities of cracked asphaltenes and straight-run asphaltenes as emulsifying agents in various petroleum products;

II. The emulsibilities of various petroleum products were determined before and after removal of the contained asphaltenes;

III. A study was made of the variation of the emulsibility of light petroleum products with increasing asphaltene concentration;

IV. A study was made of the variation of the interfacial tension of light petroleum products with increasing asphaltene concentration.

Geological Survey of the United States

The role of geologists as the scientific basis of
 water-borne pollution and investigation from a number of
 different viewpoints. The geological survey was divided
 into four parts:

I. A comparison was made of the relation of various
 geological and physical factors as well as
 climate in various petroleum provinces;

II. The distribution of various petroleum provinces
 was determined before and after removal of the geological
 factors;

III. A study was made of the variation of the amount
 of light petroleum provinces with increasing ge-
 ological complexity;

IV. A study was made of the variation of the total
 weight of light petroleum provinces with increasing
 geological complexity.

Part I. Comparison of cracked and straight-run
asphaltenes as emulsifying agents

Procedure:

A comparison was made of the emulsifying abilities of asphaltenes contained in cracked tar and those contained in straight-run asphalt. Two fuel oils were prepared so that each had a viscosity of approximately 225 S.S.U. at 122°F. The first was a blend of 70% by volume of cracked tar cut back with 30% of straight-run gas oil; this blend will be hereinafter referred to as "the cracked blend." The second was a blend of 50% by volume of straight-run asphalt cut back with 50% of straight-run gas oil; this blend will be hereinafter referred to as "the straight-run blend." All of these products were derived from California crudes. The cracked tar had a 7.2% cyclohexane insoluble content, which was determined by the method prescribed by Abraham¹⁰ for solubility tests. The per cent cyclohexane insoluble is an index of the amount of asphaltenes heavier than those found in straight run residua or, in other words, a measure of the severity of cracking.¹¹

A few drops from a 25 milliliter dropper bottle of the cracked blend were added to a petroleum product sample, such as benzene, and a like quantity of the straight-run blend added to another equal sample of the same product.

Each mixture was shaken in a 100 milliliter graduate with equal volumes of distilled water and its resistance to separation observed. This comparison of the emulsifying effect of cracked and straight-run asphaltenes was determined in benzene, cyclohexane, carbon tetrachloride, kerosene, and straight-run gas oil.

Results:

With benzene, the straight-run asphaltenes, as contained in the straight-run blend, allowed the water to separate. A small amount of emulsion was formed below the oil layer but this, too, broke upon standing. The cracked asphaltenes caused a permanent emulsion to form.

With cyclohexane containing straight-run asphaltenes, similar results were obtained as with benzene, except that a middle layer of emulsion remained while most of the water separated. With cracked asphaltenes, a heavier emulsion was formed than in the case of benzene.

With carbon tetrachloride, the straight-run asphaltenes allowed the emulsion to break, the water going to the top; a middle layer of emulsion remained. The cracked asphaltenes caused a very thick, almost solid, emulsion to form.

With kerosene, the straight-run asphaltenes formed a better emulsion than they were capable of doing in the other products tested. As expected, however, the cracked asphaltenes formed more and thicker emulsion than did the straight-run asphaltenes.

Small amounts of material are available in the following form:

[illegible][illegible]

1941

1111 Broadway, New York City, New York 10001

With straight-run gas oil, the straight-run asphaltenes allowed the water to separate while the cracked asphaltenes formed a stable emulsion.

Discussion of results:

In all cases the emulsifying effect of the cracked asphaltenes was noticeably greater than that of the straight-run asphaltenes. It was noted that equal quantities of asphaltene had varying emulsifying effect on the different products tested: the composition of the oil is a factor in emulsification, but only inasmuch as it affects the more fundamental factors of interfacial tension and sedimentation force.

With the exception of the above, the following information is being furnished to you for your information only. It is not intended to be used for any other purpose.

[illegible]

103-107

Part II. Emulsibility before and after removal
of asphaltenes

Procedure:

The effect of asphaltene content upon the emulsibility of an oil was approached by determining the emulsibility of the oil before and after the removal of the contained asphaltenes.

The emulsibility was determined by Federal Specification Method 320.32.¹² Briefly, this test consists of paddling for five minutes 27 milliliters of the oil and 53 milliliters of distilled water in a 100 milliliter graduated cylinder. The temperature of the test was 130° F. which was obtained by immersing the graduate to the 85 milliliter mark in a water bath maintained at this temperature. The speed of rotation of the paddle was 1500 revolutions per minute, which was checked by a revolution counter. At the end of five minutes the paddle was stopped and removed from the cylinder. Readings ^{of} the demarcation between the topmost oil layer and the adjoining emulsion were taken and recorded with the time of the readings. In this work the "demulsibility" was taken as the average slope of the curve obtained by plotting the volume of the oil separated versus the time since stopping the paddle. The "emulsibility" is the numerical value of the reciprocal of the "demulsibility."

1977-78, 1978-79, 1979-80, 1980-81, 1981-82, 1982-83, 1983-84, 1984-85, 1985-86, 1986-87, 1987-88, 1988-89, 1989-90, 1990-91, 1991-92, 1992-93, 1993-94, 1994-95, 1995-96, 1996-97, 1997-98, 1998-99, 1999-00, 2000-01, 2001-02, 2002-03, 2003-04, 2004-05, 2005-06, 2006-07, 2007-08, 2008-09, 2009-10, 2010-11, 2011-12, 2012-13, 2013-14, 2014-15, 2015-16, 2016-17, 2017-18, 2018-19, 2019-20, 2020-21, 2021-22, 2022-23, 2023-24, 2024-25, 2025-26, 2026-27, 2027-28, 2028-29, 2029-30, 2030-31, 2031-32, 2032-33, 2033-34, 2034-35, 2035-36, 2036-37, 2037-38, 2038-39, 2039-40, 2040-41, 2041-42, 2042-43, 2043-44, 2044-45, 2045-46, 2046-47, 2047-48, 2048-49, 2049-50, 2050-51, 2051-52, 2052-53, 2053-54, 2054-55, 2055-56, 2056-57, 2057-58, 2058-59, 2059-60, 2060-61, 2061-62, 2062-63, 2063-64, 2064-65, 2065-66, 2066-67, 2067-68, 2068-69, 2069-70, 2070-71, 2071-72, 2072-73, 2073-74, 2074-75, 2075-76, 2076-77, 2077-78, 2078-79, 2079-80, 2080-81, 2081-82, 2082-83, 2083-84, 2084-85, 2085-86, 2086-87, 2087-88, 2088-89, 2089-90, 2090-91, 2091-92, 2092-93, 2093-94, 2094-95, 2095-96, 2096-97, 2097-98, 2098-99, 2099-00, 2100-01, 2101-02, 2102-03, 2103-04, 2104-05, 2105-06, 2106-07, 2107-08, 2108-09, 2109-10, 2110-11, 2111-12, 2112-13, 2113-14, 2114-15, 2115-16, 2116-17, 2117-18, 2118-19, 2119-20, 2120-21, 2121-22, 2122-23, 2123-24, 2124-25, 2125-26, 2126-27, 2127-28, 2128-29, 2129-30, 2130-31, 2131-32, 2132-33, 2133-34, 2134-35, 2135-36, 2136-37, 2137-38, 2138-39, 2139-40, 2140-41, 2141-42, 2142-43, 2143-44, 2144-45, 2145-46, 2146-47, 2147-48, 2148-49, 2149-50, 2150-51, 2151-52, 2152-53, 2153-54, 2154-55, 2155-56, 2156-57, 2157-58, 2158-59, 2159-60, 2160-61, 2161-62, 2162-63, 2163-64, 2164-65, 2165-66, 2166-67, 2167-68, 2168-69, 2169-70, 2170-71, 2171-72, 2172-73, 2173-74, 2174-75, 2175-76, 2176-77, 2177-78, 2178-79, 2179-80, 2180-81, 2181-82, 2182-83, 2183-84, 2184-85, 2185-86, 2186-87, 2187-88, 2188-89, 2189-90, 2190-91, 2191-92, 2192-93, 2193-94, 2194-95, 2195-96, 2196-97, 2197-98, 2198-99, 2199-00, 2200-01, 2201-02, 2202-03, 2203-04, 2204-05, 2205-06, 2206-07, 2207-08, 2208-09, 2209-10, 2210-11, 2211-12, 2212-13, 2213-14, 2214-15, 2215-16, 2216-17, 2217-18, 2218-19, 2219-20, 2220-21, 2221-22, 2222-23, 2223-24, 2224-25, 2225-26, 2226-27, 2227-28, 2228-29, 2229-30, 2230-31, 2231-32, 2232-33, 2233-34, 2234-35, 2235-36, 2236-37, 2237-38, 2238-39, 2239-40, 2240-41, 2241-42, 2242-43, 2243-44, 2244-45, 2245-46, 2246-47, 2247-48, 2248-49, 2249-50, 2250-51, 2251-52, 2252-53, 2253-54, 2254-55, 2255-56, 2256-57, 2257-58, 2258-59, 2259-60, 2260-61, 2261-62, 2262-63, 2263-64, 2264-65, 2265-66, 2266-67, 2267-68, 2268-69, 2269-70, 2270-71, 2271-72, 2272-73, 2273-74, 2274-75, 2275-76, 2276-77, 2277-78, 2278-79, 2279-80, 2280-81, 2281-82, 2282-83, 2283-84, 2284-85, 2285-86, 2286-87, 2287-88, 2288-89, 2289-90, 2290-91, 2291-92, 2292-93, 2293-94, 2294-95, 2295-96, 2296-97, 2297-98, 2298-99, 2299-00, 2300-01, 2301-02, 2302-03, 2303-04, 2304-05, 2305-06, 2306-07, 2307-08, 2308-09, 2309-10, 2310-11, 2311-12, 2312-13, 2313-14, 2314-15, 2315-16, 2316-17, 2317-18, 2318-19, 2319-20, 2320-21, 2321-22, 2322-23, 2323-24, 2324-25, 2325-26, 2326-27, 2327-28, 2328-29, 2329-30, 2330-31, 2331-32, 2332-33, 2333-34, 2334-35, 2335-36, 2336-37, 2337-38, 2338-39, 2339-40, 2340-41, 2341-42, 2342-43, 2343-44, 2344-45, 2345-46, 2346-47, 2347-48, 2348-49, 2349-50, 2350-51, 2351-52, 2352-53, 2353-54, 2354-55, 2355-56, 2356-57, 2357-58, 2358-59, 2359-60, 2360-61, 2361-62, 2362-63, 2363-64, 2364-65, 2365-66, 2366-67, 2367-68, 2368-69, 2369-70, 2370-71, 2371-72, 2372-73, 2373-74, 2374-75, 2375-76, 2376-77, 2377-78, 2378-79, 2379-80, 2380-81, 2381-82, 2382-83, 2383-84, 2384-85, 2385-86, 2386-87, 2387-88, 2388-89, 2389-90, 2390-91, 2391-92, 2392-93, 2393-94, 2394-95, 2395-96, 2396-97, 2397-98, 2398-99, 2399-00, 2400-01, 2401-02, 2402-03, 2403-04, 2404-05, 2405-06, 2406-07, 2407-08, 2408-09, 2409-10, 2410-11, 2411-12, 2412-13, 2413-14, 2414-15, 2415-16, 2416-17, 2417-18, 2418-19, 2419-20, 2420-21, 2421-22, 2422-23, 2423-24, 2424-25, 2425-26, 2426-27, 2427-28, 2428-29, 2429-30, 2430-31, 2431-32,

The above is a summary of the information received from the various sources mentioned above. It is not intended to be a complete and exhaustive statement of the facts, but rather a summary of the information received from the various sources mentioned above.

— *Journal of the American Medical Association*

The committee was informed by several witnesses that the defendant had been seen at the residence of the victim on the night of the murder. The committee also received information from a confidential source that the defendant had been seen at the residence of the victim on the night of the murder. The committee is of the opinion that the defendant was present at the residence of the victim on the night of the murder.

Department of the Interior, Bureau of Land Management, Washington, D.C. 20250. The land was obtained by

of the building was 1000 revolutions per minute, which was
observed by a revolution counter. At the end of 150 minutes
the building was stopped and removed from the cylinder. The

16
 Let the Government in power and the

Do not use any of the following items in your collection: any of the following items

the magazine. In this sense, the "domestication" was below a

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also left chloride ions with salt water saturation. The salt so

The asphaltene content of the oil was determined gravimetrically by adsorbing the asphaltenes on asbestos. A Gooch crucible was carefully prepared by pouring into it a suspension of finely divided asbestos fiber, sucking it dry through a suction flask, and tapping the mat tight. This process was repeated until light could just no longer be seen through the holes of the crucible. The crucible was then dried in an air oven at 105°C . for a period of two hours, after which it was allowed to cool in a desiccator. The crucible was then weighed to 0.1 milligram. The weighed crucible was placed in the suction flask and the oil filtered through it. The weight of the oil filtered was determined by weighing the stoppered flask containing the oil before and after filtering. The crucible was again placed in the air oven at 105°C ., then cooled in the desiccator, and weighed. The difference in weight of the crucible before and after filtering was the weight of the adsorbed asphaltenes. The per cent asphaltene content of the oil was then calculated.

Results:

Sample data and calculations for these results are presented in the Appendix.

<u>Sample</u>	<u>Asphaltene content (%)</u>	<u>Emulsibility with asphaltenes (min/ml)</u>	<u>Emulsibility without asphaltenes (min/ml)</u>
Cracked gas oil	.035	.242	.111
Lab oil #1	.399	.568	.274
Lab oil #2	.695	.242	.120

The significant feature of the oil was contained therein, especially by adhering to the minimum no. 1000. A good result was actually obtained by heating the oil in a suspension of finely divided asbestos fiber, which is dry through a porous flask, and passing the oil right. The process was repeated until the oil could no longer be seen through the glass of the vessels. The crystals were then dried in an oven at 100° C. for a period of two hours, after which it was allowed to cool in a desiccator. The crystals were then weighed as 0.1 milligram. The weighed crystals were placed in the reaction flask and the oil filtered through it. The weight of the oil filtered was determined by weighing the weighed flask containing the oil before and after filtration. The crystals were then placed in the oil over at 100° C., then cooled in the desiccator, and weighed. The difference in weight of the weighed before and after filtration was the weight of the weighed substance. The two most significant results of the oil were as follows.

Results

Results are as follows for the two cases and are

shown in the appendix.

Weight of oil (gms.)	Weight of oil (gms.)	Weight of oil (gms.)	Weight of oil (gms.)
100	100	100	100
100	100	100	100
100	100	100	100

Discussion of results:

There was a definite decrease in the emulsibility after the asphaltenes were removed. The emulsibility was lessened in each case but the final emulsibility was still characteristic of the oil. If asphaltenes were the only factor affecting emulsibility, it would be expected that their removal would reduce all oils to the same level of emulsibility. The last column shows that the final emulsibility differed in each case. In other words, the emulsibility was lessened by the removal of the asphaltenes but was still dependent on the other factors influencing interfacial tension and those affecting the sedimentation force. This is also substantiated by the fact that Lab oil #2, with an asphaltene content of .695%, had a lower emulsibility than did Lab oil #1, which had an asphaltene content of .399%.

There was a further question in the early days of the
the experiment was made. The early days of the
in fact was that the first experiment was still a
kind of the oil. It was found that the oil was
being used, it was as expected and still
now the oil was still in the same level of
oil. The first experiment was still a
different in each case. In each case, the
found by the results of the experiment was still
points on the other hand, the results of the
and those affecting the results of the
indicated by the results of the experiment
of the oil, but a large quantity of oil
of which had an average content of 100.

Part III. Emulsibility versus asphaltene concentration

Procedure:

The emulsibilities of different light petroleum products were determined with increasing asphaltene concentration. The asphaltenes were added to such products as benzene in the form of the cracked blend (70% cracked tar and 30% straight-run gas oil). A representative sample of the cracked blend was placed in a 25 milliliter dropper bottle. To 27 milliliters of benzene in a 100 milliliter graduate was added a number of drops of cracked blend. The sample was mixed, 53 milliliters of distilled water added, and the emulsibility determined according to Federal Specification Method 320.32, outlined in the "Procedure" of Part II. The weight of the asphaltenes added was determined by weighing the dropper bottle before and after the addition of the asphaltenes to the sample. Strictly speaking, this was the weight of the cracked blend and not of the asphaltenes. But since the emulsibility was to be correlated with the relative asphaltene content, the weight of the cracked blend was considered representative of the relative asphaltene content. The emulsibilities of the same petroleum product with different amounts of asphaltene added were similarly determined.

These tests of variation of emulsibility with asphaltene concentration were made for benzene, cyclohexane, hexane, and straight-run gas oil. The tests were run both at 130° F. and 70° F. It will be noted that benzene, cyclohexane, and hexane contain six carbon atoms and are typical of the aromatics, naphthenes, and paraffins, respectively.

THE RELATIONSHIP BETWEEN VISCOSITY AND TEMPERATURE

Introduction

The relationship of viscosity to temperature is a subject of considerable importance in many branches of science and industry. It is a subject which has attracted the attention of many investigators, and the results of their work have been of great value in the development of many of our modern industries. The purpose of this paper is to review the work of these investigators, and to present a summary of the results of their work. The work of these investigators has been divided into two main parts: the first part deals with the relationship of viscosity to temperature in the case of liquids, and the second part deals with the relationship of viscosity to temperature in the case of gases. In the case of liquids, the relationship is generally found to be of the form $\eta = A e^{B/T}$, where η is the viscosity, A and B are constants, and T is the absolute temperature. In the case of gases, the relationship is generally found to be of the form $\eta = C T^{1/2}$, where η is the viscosity, C is a constant, and T is the absolute temperature. The results of these investigations have been of great value in the development of many of our modern industries, and they have also been of great value in the development of our knowledge of the physical properties of matter. The work of these investigators has been of such a nature that it has enabled us to understand the relationship of viscosity to temperature in a much more complete manner than we were able to do before. This has enabled us to develop many of our modern industries, and it has also enabled us to develop many of our modern scientific theories. The work of these investigators has been of such a nature that it has enabled us to understand the relationship of viscosity to temperature in a much more complete manner than we were able to do before. This has enabled us to develop many of our modern industries, and it has also enabled us to develop many of our modern scientific theories.

Results of the tests run at 130° F:

Benzene (130° F.)

No. of drops of asphaltene	Weight of asphaltene (gm)	Concentration of asphaltene (gm/liter)	Demulsibility slope (ml/min)	Emulsibility 1/slope (min/ml)
1	.029	1.07	116	.009
2	.054	2.00	22.9	.044
2	.056	2.07	20.4	.049
3	.071	2.63	12.4	.081
3	.089	3.30	18.0	.055
4	.119	4.41	6.9	.145
4	.150	5.56	3.7	.270
5	.137	5.07	5.0	.200
6	.160	5.93	6.8	.147
8	.219	7.74	3.9	.256
8	.228	8.45	3.6	.278
10	.278	10.30	2.9	.345
12	.332	12.50	2.9	.345
15	.494	18.28	1.15	.870
15	.570	21.10	1.08	.925
15	.570	21.10	1.45	.690
20	.665	24.62	1.00	1.000
25	.805	29.80	1.10	.909

Cyclohexane (130° F.)

No. of drops of asphaltene	Weight of asphaltene (gm)	Concentration of asphaltene (gm/liter)	Demulsibility slope (ml/min)	Emulsibility 1/slope (min/ml)
1	.028	1.04	4.50	.222
2	.056	2.08	2.30	.435
2	.060	2.22	1.10	.909
3	.088	3.26	.97	1.03
3	.078	2.89	.73	1.37
5	.130	4.81	.32	3.12
5	.182	5.63	.32	3.12
8	.244	9.04	.12	8.33
10	.342	12.68	.050	20.0
15	.514	19.02	.051	19.6

Table 1

No. of groups of subjects	Weight of subjects (kg)	Height of subjects (cm)	Age (years)	Sex
1	60.0	165.0	20.0	M
2	60.0	165.0	20.0	F
3	60.0	165.0	20.0	M
4	60.0	165.0	20.0	F
5	60.0	165.0	20.0	M
6	60.0	165.0	20.0	F
7	60.0	165.0	20.0	M
8	60.0	165.0	20.0	F
9	60.0	165.0	20.0	M
10	60.0	165.0	20.0	F
11	60.0	165.0	20.0	M
12	60.0	165.0	20.0	F
13	60.0	165.0	20.0	M
14	60.0	165.0	20.0	F
15	60.0	165.0	20.0	M
16	60.0	165.0	20.0	F
17	60.0	165.0	20.0	M
18	60.0	165.0	20.0	F
19	60.0	165.0	20.0	M
20	60.0	165.0	20.0	F

Table 2

No. of groups of subjects	Weight of subjects (kg)	Height of subjects (cm)	Age (years)	Sex
1	60.0	165.0	20.0	M
2	60.0	165.0	20.0	F
3	60.0	165.0	20.0	M
4	60.0	165.0	20.0	F
5	60.0	165.0	20.0	M
6	60.0	165.0	20.0	F
7	60.0	165.0	20.0	M
8	60.0	165.0	20.0	F
9	60.0	165.0	20.0	M
10	60.0	165.0	20.0	F
11	60.0	165.0	20.0	M
12	60.0	165.0	20.0	F
13	60.0	165.0	20.0	M
14	60.0	165.0	20.0	F
15	60.0	165.0	20.0	M
16	60.0	165.0	20.0	F
17	60.0	165.0	20.0	M
18	60.0	165.0	20.0	F
19	60.0	165.0	20.0	M
20	60.0	165.0	20.0	F

Hexane (130° F.)

No. of drops of asphaltene	Weight of asphaltene (gm)	Concentration of asphaltene (gm/liter)	Demulsibility slope (ml/min)	Emulsibility 1/slope (min/ml)
1	.031	1.15	110	.0091
2	.053	1.96	107	.0093
2	.054	2.00	106	.0095
4	.110	4.07	73	.0137
5	.169	6.26	36	.028
5	.180	6.67	29	.034
10	.315	11.67	26	.038
15	.455	16.85	10.4	.096
15	.532	19.71	6.0	.167
20	.685	25.38	2.3	.435

Straight-run gas oil (130° F.)

No. of drops of asphaltene	Weight of asphaltene (gm)	Concentration of asphaltene (gm/liter)	Demulsibility slope (ml/min)	Emulsibility 1/slope (min/ml)
0	0	0	31	.032
0	0	0	27	.037
0	0	0	33	.030
1	.003	.11	25	.040
1	.026	.96	8.7	.115
1	.028	1.04	8.7	.115
2	.051	1.89	3.2	.302
3	.082	3.04	.98	1.02
4	.108	4.00	.35	2.86
4	.117	4.34	.35	2.86
5	.152	5.63	.157	6.37
6	.169	6.26	.125	8.00
6	.180	6.67	.100	10.00
9	.281	10.41	.033	30.30

Table 1.1

Year	Area (ha)	Production (kg)	Yield (kg/ha)	Value (R)
1990	100	1000	10.0	1000
1991	100	1000	10.0	1000
1992	100	1000	10.0	1000
1993	100	1000	10.0	1000
1994	100	1000	10.0	1000
1995	100	1000	10.0	1000
1996	100	1000	10.0	1000
1997	100	1000	10.0	1000
1998	100	1000	10.0	1000
1999	100	1000	10.0	1000
2000	100	1000	10.0	1000
2001	100	1000	10.0	1000
2002	100	1000	10.0	1000
2003	100	1000	10.0	1000
2004	100	1000	10.0	1000
2005	100	1000	10.0	1000
2006	100	1000	10.0	1000
2007	100	1000	10.0	1000
2008	100	1000	10.0	1000
2009	100	1000	10.0	1000
2010	100	1000	10.0	1000

Table 1.2

Year	Area (ha)	Production (kg)	Yield (kg/ha)	Value (R)
1990	100	1000	10.0	1000
1991	100	1000	10.0	1000
1992	100	1000	10.0	1000
1993	100	1000	10.0	1000
1994	100	1000	10.0	1000
1995	100	1000	10.0	1000
1996	100	1000	10.0	1000
1997	100	1000	10.0	1000
1998	100	1000	10.0	1000
1999	100	1000	10.0	1000
2000	100	1000	10.0	1000
2001	100	1000	10.0	1000
2002	100	1000	10.0	1000
2003	100	1000	10.0	1000
2004	100	1000	10.0	1000
2005	100	1000	10.0	1000
2006	100	1000	10.0	1000
2007	100	1000	10.0	1000
2008	100	1000	10.0	1000
2009	100	1000	10.0	1000
2010	100	1000	10.0	1000
2011	100	1000	10.0	1000
2012	100	1000	10.0	1000
2013	100	1000	10.0	1000
2014	100	1000	10.0	1000
2015	100	1000	10.0	1000
2016	100	1000	10.0	1000
2017	100	1000	10.0	1000
2018	100	1000	10.0	1000
2019	100	1000	10.0	1000
2020	100	1000	10.0	1000

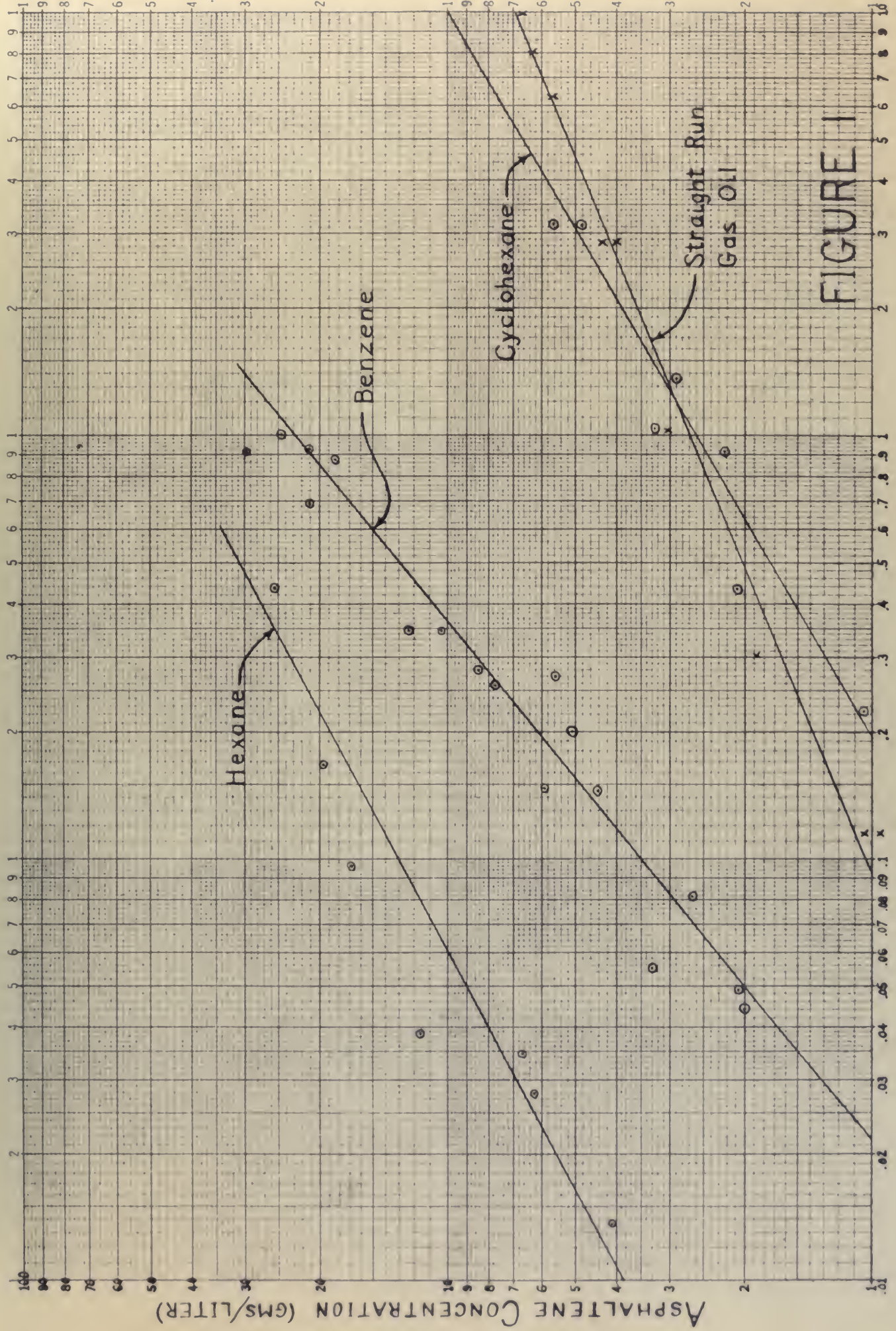


FIGURE 1

EMULSIBILITY AT 130° F. (MIN/ML)

Discussion of results of tests at 130° P:

These results when plotted on log-log paper (Figure 1) yield straight lines. All curves show definitely that as the asphaltene concentration is increased, the emulsibility also increases. The explanation of the logarithmic variation of emulsibility with asphaltene concentration is had from adsorption considerations, for the asphaltenes are adsorbed at the oil-water interface and are then in a position to lower the interfacial tension, thereby increasing the emulsibility. An emulsifying agent acts by virtue of its ability to lower the interfacial tension, but before it can affect the interfacial tension it must be adsorbed in the interface. Thus emulsibility is seen to be dependent on the adsorption of the asphaltenes in the interface.

Freundlich's¹³ empirical adsorption isotherm is

$$q = kc^n \quad (9)$$

where q is the weight of material (asphaltene) adsorbed per unit area of adsorbing interface,

c is the concentration of the adsorbed material in the continuous phase (e.g. benzene), and

k and n are constants dependent on the particular system. If the emulsibility is a linear function of the adsorption at the interface then it would follow that the emulsibility could be expressed

$$E = Kc^n \quad (10)$$

Discussion of results of tests at 150° F:

These results were plotted on log-log paper (Figure 1)

Yield strength lines. All curves show relatively flat at

the beginning of elongation, then a sharp drop in yield strength

also occurred. The comparison of the logarithmic variation

of yield strength with logarithmic elongation is not too ad-

apted to the data, but the agreement was improved as

the elongation increased and the data in a position to show

the logarithmic variation, showing increasing the sensitivity

in elongation curve with yield of the metal in lower

the logarithmic variation, but before it can affect the inter-

metal failure it must be shown in the diagram. The

relationship is seen to be dependent on the elongation of the

relationship in the diagram.

Relationship of yield strength to elongation is

$$Y = K \epsilon^n \quad (1)$$

where Y is the yield or tensile strength, K is a constant

and n is the elongation index.

n is the elongation of the elongated material in the

relationship (see Figure 1 and

Figure 2 and compare the data in the logarithmic system.

If the relationship is a linear function of the elongation as

the diagram shows it would follow that the relationship would

be expressed

$$Y = K \epsilon \quad (2)$$

This equation holds for the emulsibility-concentration relation of benzene, cyclohexane, hexane, and straight-run gas oil at 130° F. The value of k and n are both dependent on the particular petroleum product used in the emulsification; n is the slope of the log-log plot of E versus c , and K is the value of the concentration when the emulsibility equals unity.

It should be noted that the straight-run gas oil line in Figure 1 plots very close to the cyclohexane line. It might therefore be tentatively reasoned that the straight-run gas oil was largely naphthenic.

the system holds for the multiplicity-composition type-
line of course, equilibrium, states, and other-
all at 100°. The value of λ and μ are both dependent on
the relations between volume and the multiplicity
is the value of the λ - μ plot at λ equals μ , and λ is
the value of the composition when the multiplicity equals
unity.

It should be noted that the multiplicity has all been
in Figure 1 above very close to the equilibrium line. It
might therefore be fairly well assumed that the multiplicity
has all been fairly constant.

From Figure 1, it is seen that the multiplicity is
fairly constant at all points of interest. It is
fairly constant at all points of interest. It is
fairly constant at all points of interest.

It is seen from Figure 1 that the multiplicity is
fairly constant at all points of interest. It is
fairly constant at all points of interest. It is
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fairly constant at all points of interest. It is
fairly constant at all points of interest. It is
fairly constant at all points of interest.

Results of the tests run at 70° F:

Benzene (70° F.)

No. of drops of asphaltene	Weight of asphaltene (gm)	Concentration of asphaltene (gm/liter)	Demulsibility slope (ml/min)	Demulsibility 1/slope (min/ml)
1	.035	1.30	21.8	.046
3	.098	3.63	4.9	.204
8	.315	11.7	1.73	.578
10	.356	13.2	1.27	.78
10	.370	13.7	1.63	.61
20	.742	27.5	1.13	.885

Cyclohexane (70° F.)

No. of drops of asphaltene	Weight of asphaltene (gm)	Concentration of asphaltene (gm/liter)	Demulsibility slope (ml/min)	Demulsibility 1/slope (min/ml)
1	.026	.963	6.60	.151
2	.077	2.85	1.94	.515
3	.099	3.67	1.52	.658
5	.159	5.89	1.12	.892
7	.236	8.75	1.17	.855
7	.240	8.90	1.23	.812
8	.250	9.26	1.25	.800
10	.314	14.3	.84	1.19
15	.477	17.7	.95	1.05

Hexane (70° F.)

No. of drops of asphaltene	Weight of asphaltene (gm)	Concentration of asphaltene (gm/liter)	Demulsibility slope (ml/min)	Demulsibility 1/slope (min/ml)
1	.029	1.07	150	.0067
4	.168	6.22	125	.0080
8	.304	11.3	117	.0085
12	.501	18.6	96	.0104
18	.666	24.7	88	.0113
24	.943	34.9	67	.0149
30	1.137	42.1	58	.0172

Table 1. (continued)

No. of cases of disease	Weight of specimen (g)	Weight of specimen (g)	Weight of specimen (g)
1	100	100	100
2	100	100	100
3	100	100	100
4	100	100	100
5	100	100	100
6	100	100	100

Table 2. (continued)

No. of cases of disease	Weight of specimen (g)	Weight of specimen (g)	Weight of specimen (g)
1	100	100	100
2	100	100	100
3	100	100	100
4	100	100	100
5	100	100	100
6	100	100	100
7	100	100	100
8	100	100	100
9	100	100	100
10	100	100	100
11	100	100	100

Table 3. (continued)

No. of cases of disease	Weight of specimen (g)	Weight of specimen (g)	Weight of specimen (g)
1	100	100	100
2	100	100	100
3	100	100	100
4	100	100	100
5	100	100	100
6	100	100	100
7	100	100	100
8	100	100	100
9	100	100	100
10	100	100	100

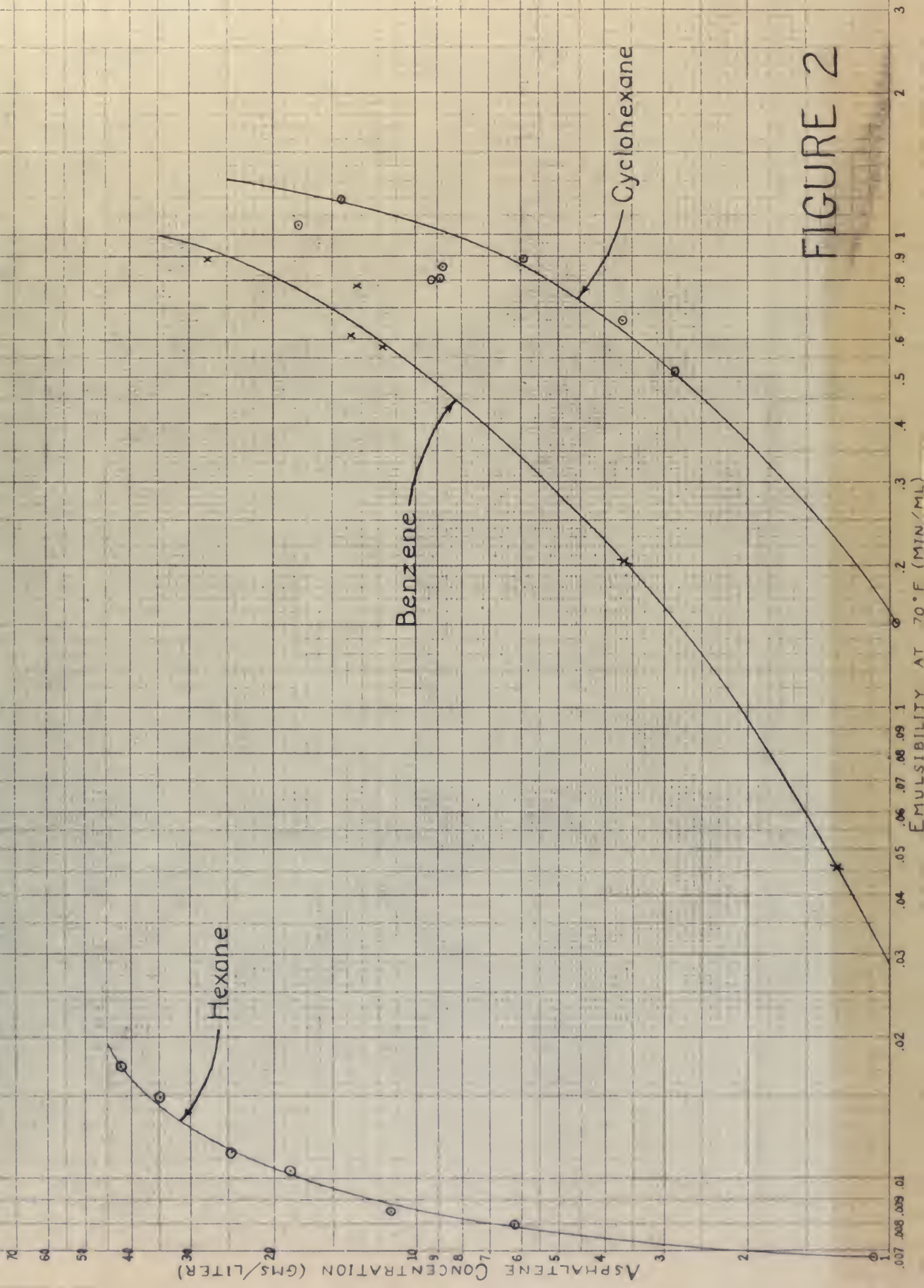
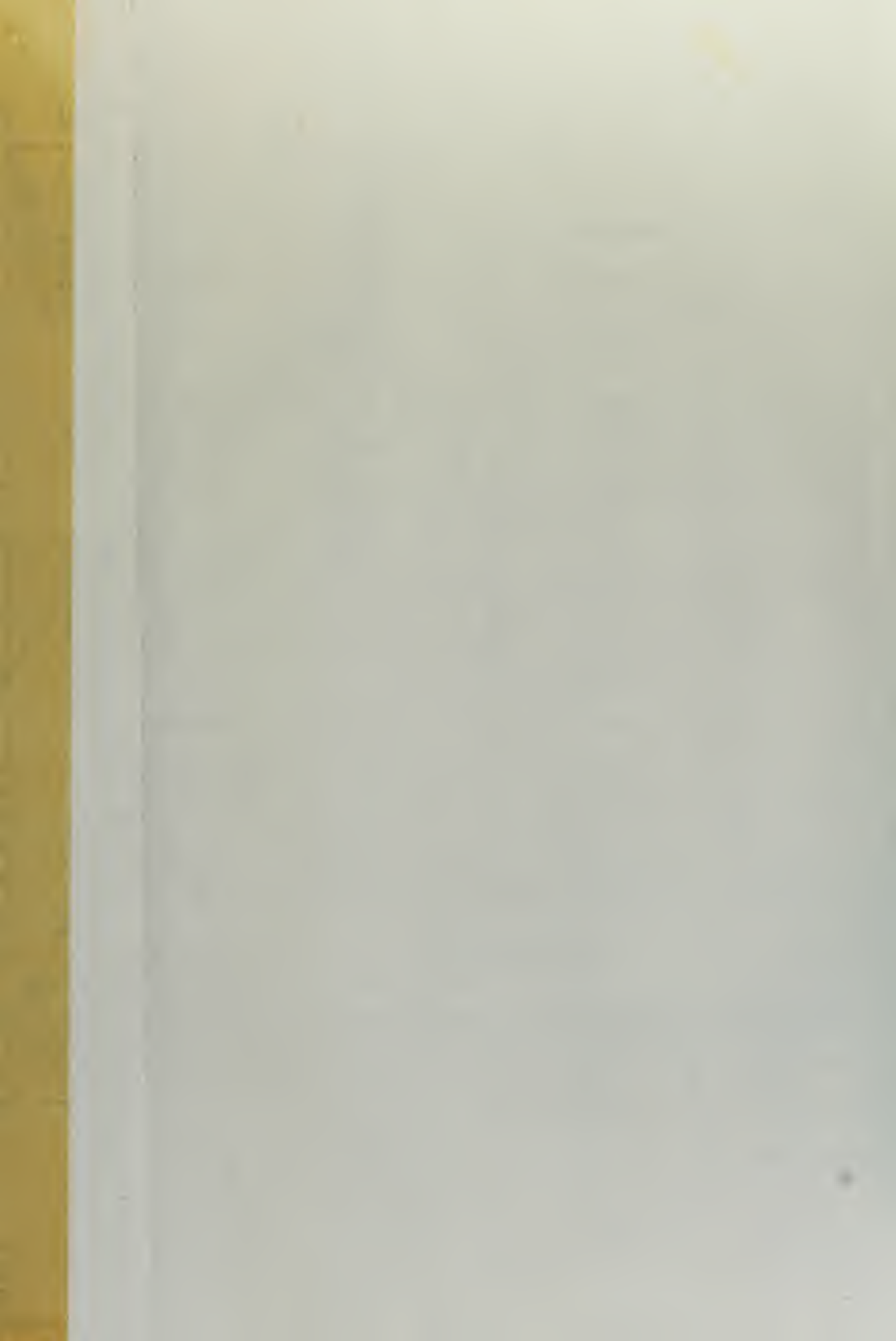


FIGURE 2



Discussion of results of tests at 70° F:

These results for the tests run at 70° F. are plotted in Figure 2. Again is shown the increase of emulsibility with increase of asphaltene concentration. At higher concentrations the emulsibility appears to approach a maximum value asymptotically.

It should be understood that the Freundlich adsorption equation is an empirical one and, as it happens, only applies under special circumstances. An empirical equation which holds more generally was developed by Langmuir:¹⁴

$$w = \frac{ac}{1 + ac} \quad (11)$$

where, applying it to the system under consideration,

w is the mass of asphaltene adsorbed per unit area of interface,

c is the concentration of the adsorbate (asphaltene) in the continuous phase (e.g., cyclohexane), and

a is a constant dependent on the particular system.

Again, if the emulsibility is a linear function of the adsorption in the interface, we can express the emulsibility:

$$E = \frac{Ac}{1 + Ac} \quad (12)$$

This relation holds better at 70° F. than does the Freundlich equation. It might be inferred that the Freundlich equation holds at raised temperatures.

Calculation of results at level of 70° F.

These results for the level of 70° F. are plotted in Figure 2. Again it shows the increase of sensitivity with increase of resistance coefficient α . At higher resistance the sensitivity appears to approach a maximum value asymptotically.

It should be understood that the theoretical equation is an idealized one and, as it happens, only applies under special circumstances. In practical systems which have some gravity, as developed by Langmuir,¹²

$$(11) \quad w = \frac{20}{1 + 2\alpha}$$

where, w is the ratio of the system order number, α is the ratio of the system order number to the mass of the system, α is the ratio of the system order number to the mass of the system, α is the ratio of the system order number to the mass of the system.

α is the ratio of the system order number to the mass of the system, α is the ratio of the system order number to the mass of the system, α is the ratio of the system order number to the mass of the system, α is the ratio of the system order number to the mass of the system, α is the ratio of the system order number to the mass of the system, α is the ratio of the system order number to the mass of the system.

$$(12) \quad w = \frac{20}{1 + 2\alpha}$$

The relative order number at 70° F. from the theoretical equation. It might be inferred that the theoretical equation holds at raised temperatures.

Part IV. Interfacial tension versus asphaltene concentration

Procedure:

The interfacial tensions of benzene, cyclohexane, and hexane with various concentrations of asphaltene were measured. The asphaltenes, in the form of the cracked blend, were added drop-wise as before from a dropper bottle, the bottle being weighed before and after addition of the asphaltene. The interfacial tension was measured by the standard drop-volume method developed by Harkins and Brown.¹⁵ Sixty-five milliliters of the solvent being tested were mixed with a weighed amount of asphaltene in a weighing bottle. A capillary tube, whose tip had been ground and polished to a known diameter, was immersed in the solvent. Distilled water was caused to flow through the capillary and a drop of water was very gradually blown up on the immersed end of the tube. Just before the drop broke away from the tip, it was allowed to build up of itself under the pull of gravity. The volume of the drop, which was determined by burette measurements, was taken for a number of drops and the average volume computed. The interfacial tension was then calculated from the following formula:

$$\sigma = \frac{V \Delta \rho g}{2 \pi r \psi(r/V^{1/3})} \quad (13)$$

where σ is the interfacial tension in dynes/cm,

V is the volume of the drop in cm^3 ,

$\Delta \rho$ is the difference in density in gm/cm^3 between the density of the water and that of the solvent mixture,

g is the gravitational constant in cm/sec^2 ,

r is the radius of the tip in cm ,

$\psi(r/v^{1/3})$ is a correction factor obtained from the reference literature.¹⁵

All measurements were made at 70°F .

Results:

Sample data and calculations of the interfacial tension are presented in the Appendix.

Benzene (70°F .)

No. of drops of asphaltene	Weight of asphaltene (gm)	Concentration of asphaltene (gm/liter)	Volume of drop (cm^3)	Interfacial tension (dynes/cm)	(dynes/cm)
0	0	0	.496	32.50	0
1	.031	.477	.472	31.00	1.50
4	.141	2.17	.398	26.50	6.00
8	.311	4.79	.383	25.50	7.00
15	.588	9.07	.366	24.43	8.07

Cyclohexane (70°F .)

No. of drops of asphaltene	Weight of asphaltene (gm)	Concentration of asphaltene (gm/liter)	Volume of drop (cm^3)	Interfacial tension (dynes/cm)	(dynes/cm)
0	0	0	.368	45.20	0
1	.040	.611	.265	33.20	12.00
2	.082	1.26	.246	30.90	14.30
4	.163	2.50	.230	28.85	16.35
8	.378	5.81	.214	27.07	18.13

$\sqrt{12\sqrt{2}}$ is a correction factor obtained from the
 9 in the region of the fly in the
 2 in the position of the fly in the

All measurements were made at 20°C.

TABLE 1

Results from the determination of the relative humidity
 and temperature in the laboratory.

TABLE 1 (continued)

No. of groups of specimens	Weight of specimens (gms)	Weight of specimens (gms)	Volume of specimens (cc)	Relative humidity (%)	Temperature (°C)
0	0	0	0	0	0
1	100	100	100	100	100
2	100	100	100	100	100
3	100	100	100	100	100
4	100	100	100	100	100
5	100	100	100	100	100

TABLE 1 (continued)

No. of groups of specimens	Weight of specimens (gms)	Weight of specimens (gms)	Volume of specimens (cc)	Relative humidity (%)	Temperature (°C)
0	0	0	0	0	0
1	100	100	100	100	100
2	100	100	100	100	100
3	100	100	100	100	100
4	100	100	100	100	100
5	100	100	100	100	100

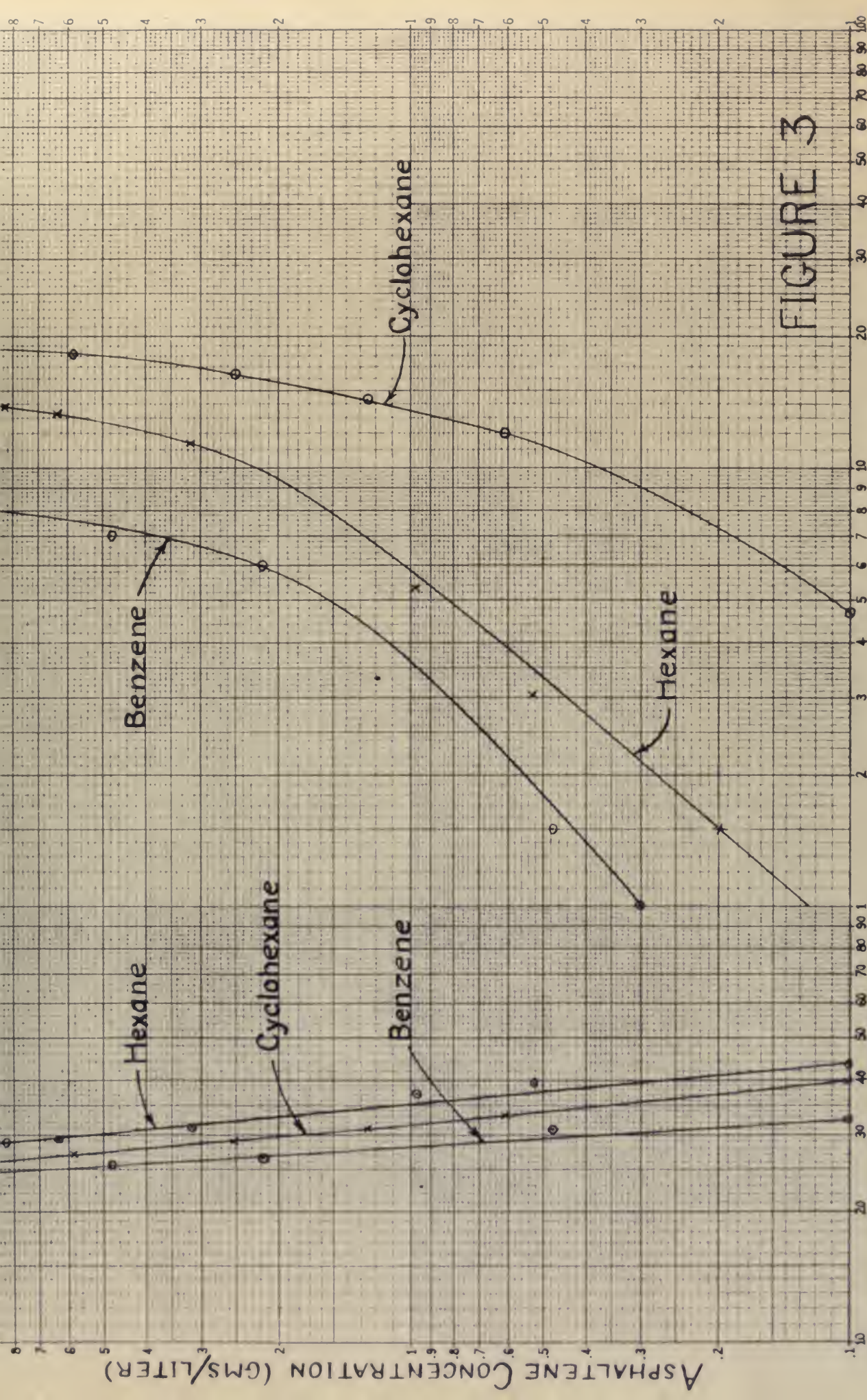


FIGURE 3

INTERFACIAL TENSION, σ
(DYNES/CM)

CHANGE OF INTERFACIAL TENSION, $\sigma_0 - \sigma$ (DYNES/CM)

Hexane (70° F.)

No. of drops of asphaltene	Weight of asphaltene (gm)	Concentration of asphaltene (gm/liter)	Volume of drop (cm ³)	Interfacial Tension (dynes/cm)	(dynes/cm)
0	0	0	.219	42.53	0
1	.034	.523	.203	39.50	3.03
2	.063	.970	.191	37.20	5.33
6	.205	3.15	.159	31.15	11.38
12	.413	6.35	.149	29.20	13.33
16	.542	8.35	.147	28.80	13.73

Discussion of results:

In all cases the interfacial tension decreased with increase of asphaltene concentration. In Figure 3 is a log-log plot of the interfacial tension versus the asphaltene concentration. The straight lines obtained indicate that the interfacial tension is a linear function of the logarithm of the asphaltene concentration. This parallels the findings of Milner¹⁶ who measured surface tensions. He found that when substances which strongly depress the surface tension are added to water, the surface tension is a linear function of the logarithm of the concentration of the dissolved substance for all except very dilute solutions.

In Figure 3 is also plotted the change of interfacial tension, $\sigma_0 - \sigma$, against the asphaltene concentration. It will be noted that the interfacial tension of cyclohexane is more affected by the addition of asphaltene than are the interfacial tensions of the other solvents. This would account

TABLE I

De. of Group of experiments	Height of experiments (cm)	Height of experiments (cm)	Volume of experiments (cm ³)	Temperature (°C)	Time (min)
0	0	0	0.10	20.20	0
1	0.004	0.004	0.004	20.10	1.00
2	0.008	0.008	0.008	20.00	2.00
3	0.012	0.012	0.012	19.90	3.00
4	0.016	0.016	0.016	19.80	4.00
5	0.020	0.020	0.020	19.70	5.00
6	0.024	0.024	0.024	19.60	6.00

Measurement of results:

In all cases the experimental results showed with in-
crease of experimental concentration. In Figure 1 is a log-log
plot of the experimental results versus the experimental concentra-
tion. The straight lines obtained indicate that the experimental
results are a linear function of the logarithm of the experimental
concentration. This indicates the validity of the experimental
measured results. The results show that when concentration
which strongly depends on the experimental results are added to water,
the results remain in a linear function of the logarithm of
the concentration of the dissolved substance. For all cases
very little variation.

In Figure 2 is also plotted the change of experimental
results, $\sigma - \sigma_0$, against the experimental concentration. It
will be noted that the experimental results of experiments
are more affected by the addition of experiments than are the
experimental results of the other experiments. This would account

for the greater emulsibility of cyclohexane as indicated in Figures 1 and 2. Also favoring the emulsibility of cyclohexane is the fact that the density differential between cyclohexane and water is not excessive ($\rho = .219 \text{ gm/cm}^3$): the less the pull of gravity, the easier it is for the diffusional force to overcome gravity and for a system to remain emulsified.

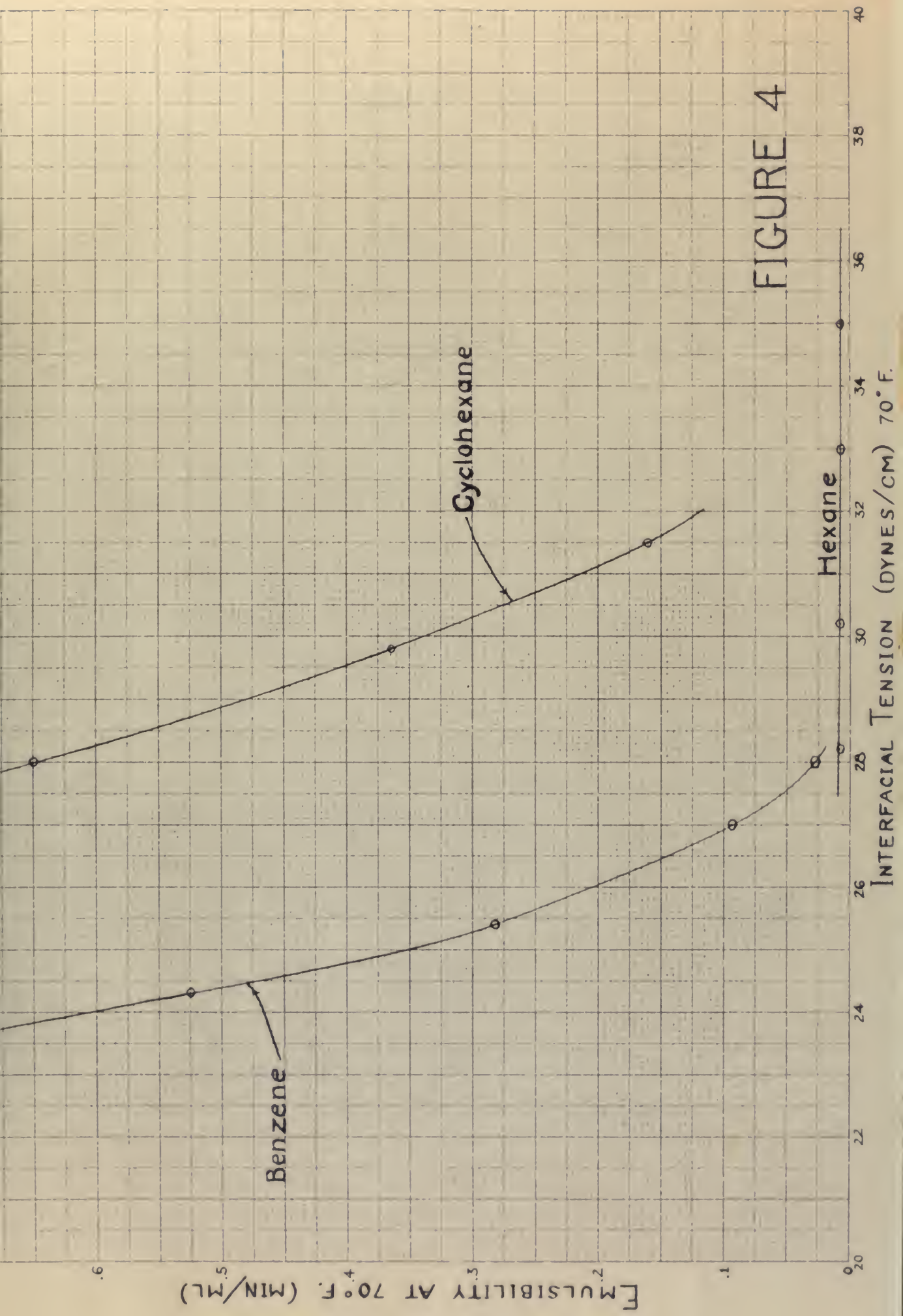
As manifest in Figure 3, the interfacial tension of hexane is more influenced by the addition of asphaltene than is the interfacial tension of benzene, although benzene is more easily emulsified than is hexane. This would seem to be a contradiction until we consider that the density differential between benzene and water ($\rho = .119 \text{ gm/cm}^3$) is very low while that between hexane and water ($\rho = .337 \text{ gm/cm}^3$) is very high. In other words, the light gravity of hexane is the predominant factor that makes hexane difficult to emulsify. Benzene, on the other hand, has a relatively heavy gravity and is more susceptible to emulsification by the lowering of the interfacial tension than is hexane. With cyclohexane, which has an intermediate gravity, the dominant factor is the comparatively great decrease of interfacial tension effected by the addition of asphaltene; it is this decrease of interfacial tension which makes cyclohexane more prone to emulsification than either benzene or hexane.

By entering Figures 2 and 3 with values of asphaltene concentration, corresponding values of emulsibility and interfacial tension have been obtained as follows:

For the greater availability of specimens as indicated in
 Figures 1 and 2. Also showing the availability of spec-
 imens in the fact that the density differential between
 specimens and water is not excessive: $\rho = 1.10 \text{ g/cm}^3$;
 the fact the bulk of gravity the water is in the air-
 filled form to measure gravity and for a water to remain
 available.

As indicated in Figure 3, the differential tension of water
 is now reflected by the addition of atmospheric air in the
 differential tension of water, although tension is more easily
 available than in water. This would seem to be a conse-
 quence of the fact we consider that the density differential be-
 tween water and water $\rho = 1.10 \text{ g/cm}^3$ is very low while
 that between water and water $\rho = 1.10 \text{ g/cm}^3$ is very high.
 In other words, the differential tension of water is the predominant
 factor that makes water available in water. However, as
 the water level, the differential tension, gravity and is now
 available in water, the differential tension of the water
 differential tension of water. This differential tension has
 an inverse effect, the differential tension is the opposite
 effect of water in water, the differential tension affected by the
 addition of atmospheric air is the difference of differential
 tension which makes differential tension more available to
 available water in water.

By adding Figures 1 and 2 with values of atmospheric con-
 ditions, atmospheric tension of availability and differential
 tension have been obtained as follows:



<u>Benzene</u>		
<u>Concentration</u> <u>(gm/liter)</u>	<u>Emulsibility</u> <u>(min/ml)</u>	<u>Interfacial tension</u> <u>(dynes/cm)</u>
1.0	.029	28.0
2.0	.094	27.0
5.0	.282	25.4
10.0	.525	24.3
<u>Cyclohexane</u>		
1.0	.160	31.5
2.0	.364	29.8
5.0	.776	27.3
10.0	1.06	25.9
<u>Hexane</u>		
1.0	.0067	35.0
2.0	.0070	33.0
5.0	.0077	30.2
10.0	.0086	28.2

The above values of emulsibility and interfacial tension are plotted in Figure 4. It is evident from these curves that the emulsibility of benzene and cyclohexane are affected by change of interfacial tension, whereas with hexane a change of interfacial tension affects the emulsibility only slightly.

<u>Interfacial tension</u> (dyne/cm)	<u>Emulsifying</u> (mg/l)	<u>Concentration</u> (mg/l)
0.00	0.00	0.1
0.04	0.04	0.2
0.08	0.08	0.3
0.12	0.12	0.4
<u>Emulsifying</u>		
0.16	0.16	0.5
0.20	0.20	0.6
0.24	0.24	0.7
0.28	0.28	0.8
<u>Emulsifying</u>		
0.32	0.32	0.9
0.36	0.36	1.0
0.40	0.40	1.1
0.44	0.44	1.2

The above values of emulsifying and interfacial tension are plotted in Figure 4. It is evident from these curves that the emulsifying of emulsion and systems are affected by change of interfacial tension, however with some change of interfacial tension affects the emulsifying only slightly.

Conclusions

1. Petroleum products containing cracked asphaltenes have greater emulsibilities than those containing straight-run asphaltenes, all other things being equal.

2. The composition of the oil is a factor in emulsibility but only inasmuch as it affects the primary factors of interfacial tension and sedimentation force.

3. The emulsibility of an oil can be lessened by removal of the asphaltenes. The resultant emulsibility will still be dependent on the other factors affecting the interfacial tension and those affecting the sedimentation force.

4. The emulsibility increases with increase of asphaltene concentration: at 130° F. according to

$$E = Kc^n \quad (10)$$

and at 70° F. according to

$$E = \frac{Ac}{1 + Ac} \quad (12)$$

These are empirical adsorption equations. They are applicable to emulsibility because the asphaltene is adsorbed in the oil-water interface, where, by the nature of the molecule, it lowers the interfacial tension, thereby making the colloidal water particles thermodynamically more stable and less able to coalesce.

5. The interfacial tension decreases with increase of asphaltene concentration; it is a linear function of

Conclusions

1. Theoretical problems involving steady-state conditions have been considered. It has been shown that the rate of change of the concentration of the oil is a function of the rate of change of the concentration of the water.

2. The concentration of the oil is a function of the rate of change of the concentration of the water. It is shown that the rate of change of the concentration of the oil is a function of the rate of change of the concentration of the water.

3. The concentration of the oil is a function of the rate of change of the concentration of the water. It is shown that the rate of change of the concentration of the oil is a function of the rate of change of the concentration of the water.

4. The concentration of the oil is a function of the rate of change of the concentration of the water. It is shown that the rate of change of the concentration of the oil is a function of the rate of change of the concentration of the water.

(10)
$$x = \frac{1}{2} \left(\frac{1}{1 + \frac{1}{2} \frac{dx}{dt}} \right)$$
 and at 70° F. according to

(11)
$$x = \frac{1}{2} \left(\frac{1}{1 + \frac{1}{2} \frac{dx}{dt}} \right)$$

These are empirical equations. They are valid only for the conditions under which the experiments were conducted. It is not possible to derive a general equation for the rate of change of the concentration of the oil as a function of the rate of change of the concentration of the water. The rate of change of the concentration of the oil is a function of the rate of change of the concentration of the water.

5. The theoretical problems involving steady-state conditions have been considered. It has been shown that the rate of change of the concentration of the oil is a function of the rate of change of the concentration of the water.

the logarithm of the concentration except for very dilute concentrations.

6. Cyclohexane (and perhaps the naphthalenes in general) is most susceptible, of the solvents tested, of emulsification by addition of asphaltenes.

7. The light gravity of hexane is the predominant factor that makes hexane difficult to emulsify.

the majority of the population have for very little

possessions.

It is therefore (and perhaps the evidence is against)

is much more likely, of the evidence being, of course,

also by means of other means.

It is the first of these in the present case.

that would seem to be the only one.

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Epilogue

The question of emulsions cannot be resolved by saying that one factor, or even two or three, are solely responsible for the formation of an emulsion. There are many factors which contribute to an emulsion, even one of the most simple type.

But we can attempt to clarify the picture by classifying these factors either as primary factors, those which directly affect the emulsibility, or as subordinate factors, those which affect the emulsibility only inasmuch as they influence the primary factors. Figure 5 is a diagrammatic sketch showing the subordination of certain factors to the primary factors.

Outline

The question of existence cannot be resolved by any-
ing that we know, or even that we know, and only we-
speculate for the purpose of an analysis. There are many
features which contribute to an analysis, even one of the
most simple ones.

Let us now attempt to clarify the status of objects.
Let us first consider the status of objects, then we shall
directly attack the possibility of an objective reality.
Some other things are possible only because we have
between the things themselves. There is a difference
between things, the relationship of things to the
things themselves.

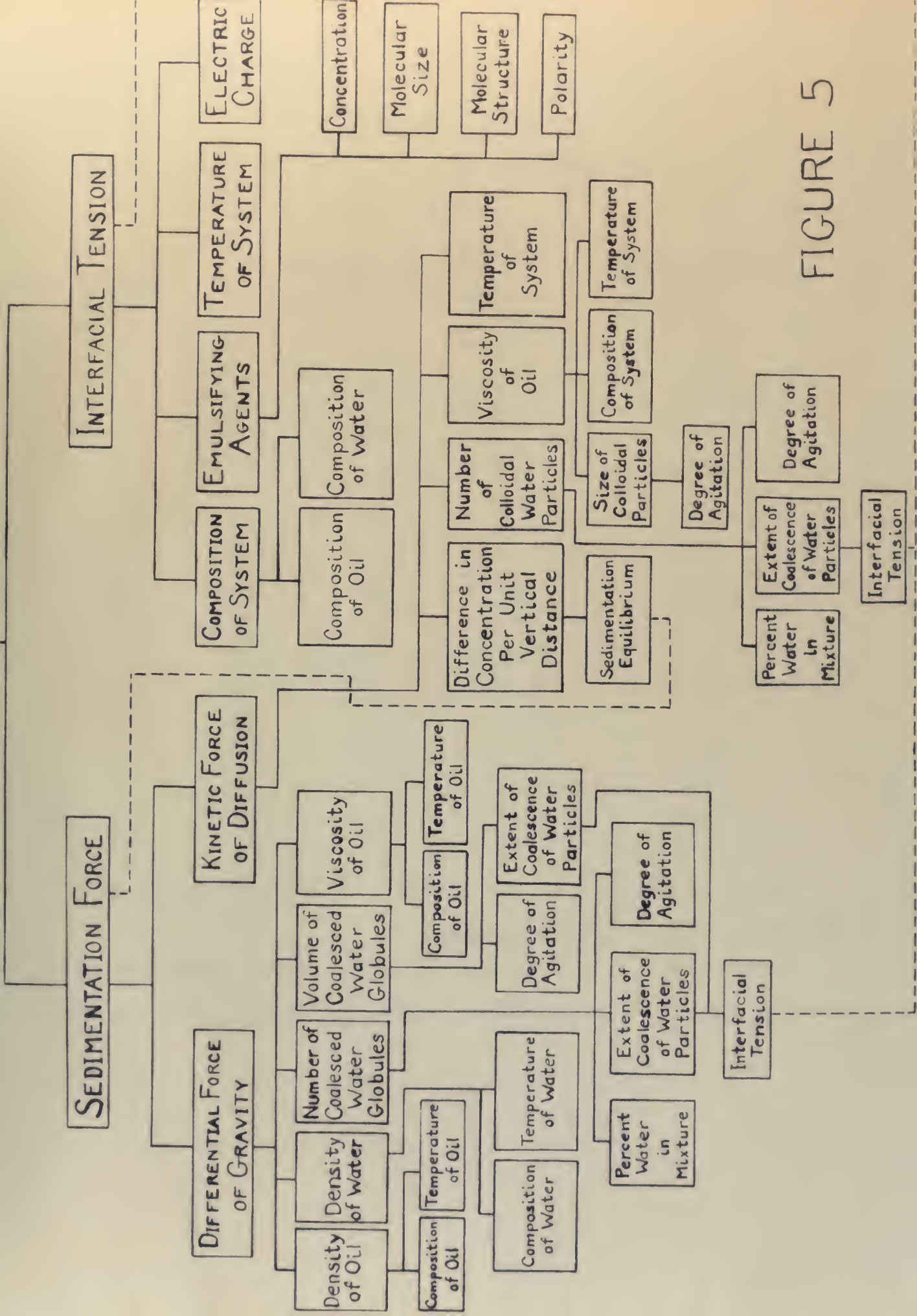


FIGURE 5

AppendixEmulsibility test (130° F.) of cracked gas oil:Before filtering

<u>Time since stopping paddle (min)</u>	<u>Reading at interface between oil and emulsion</u>	<u>Oil settled out (mls)</u>
0	80.7	0
1	78.0	2.7
2	74.0	6.7
3	68.8	11.9
4	63.7	17.0
5	58.9	21.8
6	55.8	24.9

After filtering

0	80.3	0
1	72.3	8.0
2	61.9	18.4
3	52.7	27.6

These data are plotted in Figure 6 from which is obtained:

	<u>Before filtering</u>	<u>After filtering</u>
Demulsibility (average slope)	4.12 ml/min	9.0 ml/min
Emulsibility (1/demulsibility)	.242 min/ml	.111 min/ml

AppendixPenetration test (ASTM D-5) of washed and oilBefore filtering

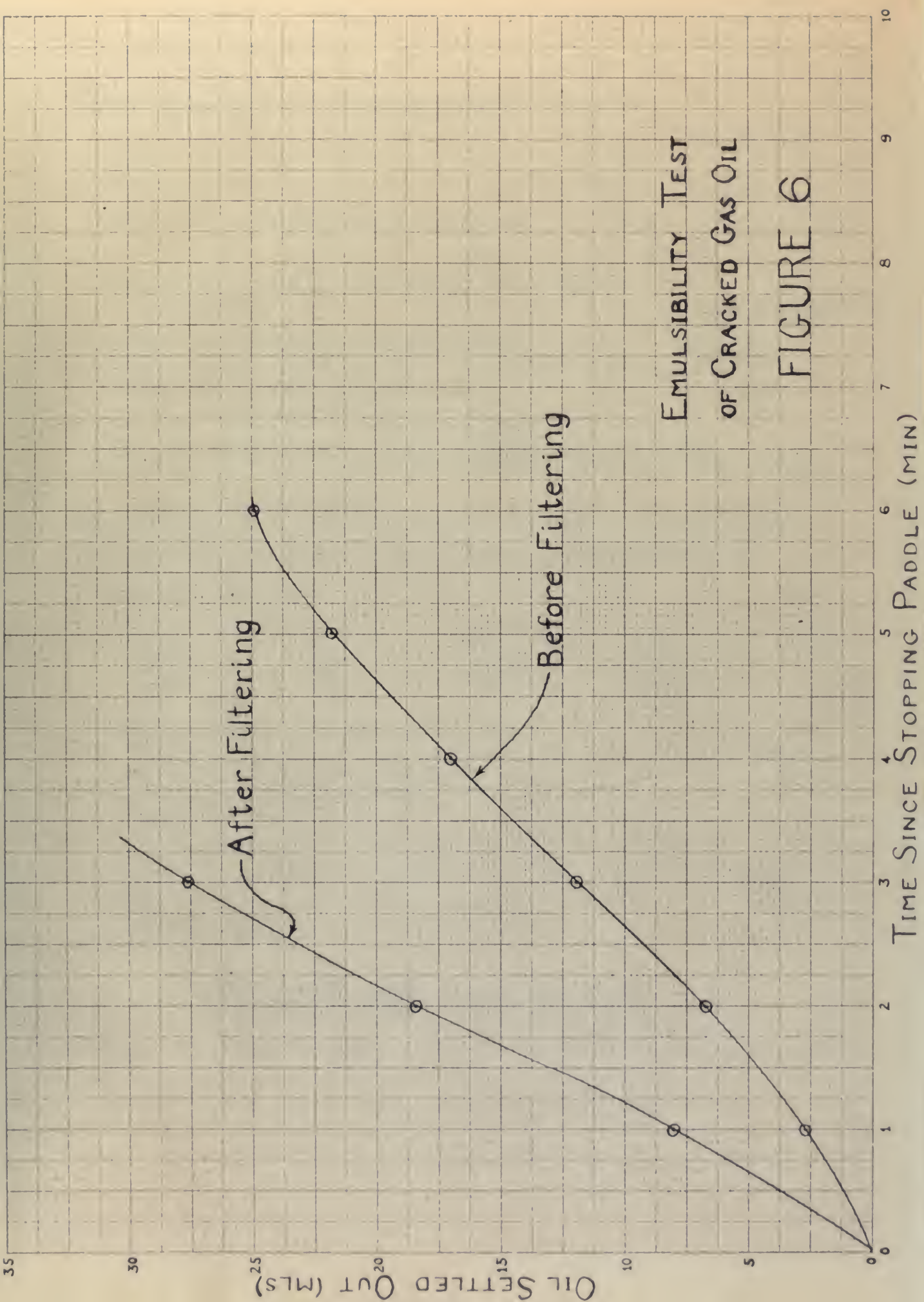
Time since stopping pump (min)	Penetration at intervals between oil and emulsion	Oil settled out (min)
0	20.7	0
1	20.0	2.7
2	20.0	6.7
3	20.2	11.0
4	20.7	17.0
5	20.8	21.2
6	20.8	24.0

After filtering

0	20.2
1	20.7
2	21.0
3	21.7

These data are plotted in Figure 2 from which is obtained:

<u>Before filtering</u>	<u>After filtering</u>
Penetration (average slope) 4.15 m/min	2.0 m/min
Penetration (Penetration) 20.8 m/min	21.1 m/min



EMULSIBILITY TEST
OF CRACKED GAS OIL

FIGURE 6

Determination of per cent asphaltene content:

Weight of cracked gas oil and flask (before)	246.39 gm.
Weight of cracked gas oil and flask (after)	<u>159.75</u>
Weight of cracked gas oil filtered	86.64
Weight of crucible, asbestos, and filtered asphaltene	21.5985 gm.
Weight of crucible and asbestos	<u>21.5684</u>
Weight of filtered asphaltene	.0301

$$\text{Per cent asphaltene content} = \frac{.0301}{86.64} \times 100 = .035\%$$

Calculation of interfacial tension at 70° F. between water and benzene containing 8 drops (.311 gm) of asphaltene:

Burette readings:

1.063	.862	1.249	1.260
<u>.686</u>	<u>.476</u>	<u>.862</u>	<u>.878</u>
.377	.386	.387	.382

Average volume of drop = .383 cm³.

$$\Delta\rho = .998 - .879 = .119 \text{ gm/cm}^3.$$

$$g = 980 \text{ cm/sec}^2.$$

$$r = .4475 \text{ cm.}$$

$$r/V^{1/3} = .616$$

$$\psi(r/V^{1/3}) = .6225$$

$$\sigma = \frac{.383 \times .119 \times 980}{2 \times .4475 \times .6225} = 25.50 \text{ dynes/cm.}$$

Calculation of gas heat capacities constant

Weight of oxygen gas at 1 liter = 1.43 gm.
 Weight of oxygen gas at 1 liter (after) = 1.39 gm.
 Weight of oxygen gas at 1 liter = 1.43 gm.

Weight of oxygen, nitrogen, and hydrogen
 Weight of oxygen and hydrogen
 Weight of nitrogen and hydrogen

$$\text{For unit molecular weight} = \frac{1.43}{1.43} \times 100 = 100\%$$

Calculation of molecular weight at 100° F. between water

and between nitrogen & oxygen (1.43 gm) at equilibrium:

Partial pressures

1.43	1.43	1.43	1.43
1.43	1.43	1.43	1.43
1.43	1.43	1.43	1.43

Average volume of 100° F. = 1.43 gm.

$$\Delta q = 1.43 \times 100 = 143 \text{ cal/mole}$$

$$k = 1.43 \text{ cal/mole}$$

$$r = 1.43 \text{ cal/mole}$$

$$v^{1/2} = 1.43$$

$$\psi(v^{1/2}) = 1.43$$

$$v = \frac{1.43 \times 100}{1.43} = 100 \text{ cal/mole}$$

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